FY 2011

Report Information

Name: ROBERT TUTTLE
Organization: SAGINAW VALLEY STATE UNIVERSITY
Email: rtuttle@svsu.edu

Contract Information
Contract Number: N000140811052
Contract Title: Solidification Based Grain Refinement in Steels
Program Officer: William Mullins
CO-PI Information:

- None

Abstract
The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for the examined grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

Fiscal year 2011 was the final year for this project. Efforts centered on completing the final three tasks in the project (Tasks 7-9). An industrial trial on an investment casting was done using rare earth silicide additions in a furnace prior to pouring (Task 7). Some of the test parts had a finer structure than the baseline castings. A series of thermal analysis experiments were conducted to evaluate prospective heterogeneous nucleation phases (Task 8). Based on undercooling measurements several candidate phases had acted as effective nuclei. Plate castings using the heterogeneous nucleation phases identified by the thermal analysis experiments were created to provide a more detailed and industrially realistic experimental situation (Task 9). These plates were sectioned into tensile and metallographic samples. Most of the powder additions were ineffective at refining the microstructure or improving mechanical properties. Due to results from the previous work in plain carbon steels, rare earth and titanium additions were also examined. Rare earth additions were found in all cases to improve the ultimate tensile strength of 304, but not necessarily the yield strength. Titanium additions were found to be ineffective at the levels employed in this work.

Technical Section

Technical Report File: N0001408110521.doc Cleared for Public Release

Slide File: N0001408110521.ppt

Progress Statement
Tasks 7 through 9 were the primary focus of fiscal year 2011 efforts. An industrial trial using 0.2% target rare earth (TRE) additions was conducted on a 1025 investment casting (Task 7). One casting on the test tree had a finer structure than the baseline casting; however, the other casting on the same tree had no observable microstructural differences. Analysis of the inclusions and fluid flow found the casting with no change had a more turbulent filling that resulted in inclusions with a different composition than the refined casting. Thermal analysis experiments using phases identified using crystallographic data as potential heterogeneous nuclei were

performed in Task 8. These experiments examined the cooling profile of a test cup and the resulting microstructure of that cup. Several potential candidates were observed to reduce the undercooling required to initiate solidification. The final experimental series conducted during this fiscal year were plate castings (Task 9). Plate castings were produced with powder additions of the phases identified in Task 8. None of the powder addition plate castings produced a noticeable difference in microstructure or mechanical properties. Based upon experimental results from the plain carbon portion of the project, rare earth and titanium additions were examined. Titanium additions produced no noticeable changes. Rare earth additions increased ultimate tensile strength in all cases, and also improved yield strength in some cases.

Refereed Journal Articles

- Article: Tuttle, R.B., "Role of Titanium on the Grain Refinement of 1030 Steel Castings," Proceedings of the 115th
  Metalcasting Congress, Schaumburg, IL

  Date: April, 2011 Status: Published
- Article: Tuttle, R.B., "Examination of Steel Castings for Potential Nucleation Phases," International Journal of Metalcasting, Vol. 3, No. 3, pp. 17-25, 2010

  Date: June, 2010 Status: Published
- Article: Tuttle, R.B., "Industrial Trial of RE Refinement in a Steel Casting," International Journal of Metalcasting
  Date: April, 2011 Status: Submitted
- Article: Tuttle, R.B., "Effect of Rare Earth Additions on the Grain Refinement of Low Carbon Steels," International Journal of Metalcasting
  Date: May, 2011 Status: Submitted
- Article: Tuttle, R.B., "Thermal Analysis Study of Heterogeneous Nuclei in Stainless Steels," International Journal of Metalcasting
  Date: May, 2011 Status: Submitted
- Article: Tuttle, R.B., "Effect of NbO Additions on the Grain Size of 1010 Steel Castings,"Materials Science and Engineering A
  Date: March, 2011 Status: Submitted

Books And Chapters

- None

Technical Reports

- None

Contributed Presentations

- Description: "Role of Titanium on the Grain Refinement of 1030 Steel Castings," 115th Metalcasting Congress, Schaumburg, IL
  Date: April, 2011

Patents

- None

Honors

- Recipient: Robert Tuttle
  Recipient Institution: Saginaw Valley State Univeristy
  Description: The presentation titled, " A Gage R&R Study of the ASTM A609 Ultrasonic Testing Standard," was one of the top five highest rated presentations at the 2011 Metalcasting Congress by conference attendees.
  Date: June, 2011

Related Sponsored Work

- Title: Machinability of FeMnAl Alloys
  Description: Major Ryan Howell who is part of the Army Research Laboratory developed a new class of iron-manganese-aluminum alloys as part of his doctoral work. These alloys have an approximate chemistry of 30% Mn, 10% Al, 1% C, and 1% Si. The high manganese and aluminum content of these alloys ensures an austenitic structure at room temperature. Unlike traditional steels, these FeMnAl alloys develop strength through the precipitation of carbide particles. The resulting mechanical properties can be strengths of 2,000 MPa, 80% elongation, and Charpy impact values of 221J. In 2009 these alloys passed ballistic testing for MIL-PRF-32269 perforated armor. The FeMnAl alloys are 12-18% lighter than low alloy steels and have significantly lower cost than current advanced high strength steels (AHSS). The high specific strength of these alloys makes these steels very attractive for a wide variety of military and transportation applications.

  One impediment to employing these alloys is a lack of knowledge about their machinability. No data on machining these new alloys has been published. The goal of this project is to conduct a basic study of the machinability of FeMnAl alloys. This project will also enable the development of cutting parameters and tooling geometry appropriate for these steels.
  Start Date: 11/1/2010 End Date: 10/31/2011

ONR Statistics

Grad Students(total):	0
PI/Co-PI Women:	0
PI/Co-PI Minority:	0
Grad Students Women:	0
Grad Students Minority:	0
Post Docs Students:	0
Post Doc Women:	0

Post Doc Minority:	0
Under Grad Students(total:	3
Under Grad Students Women:	1
Under Grad Students Minority:	0
Degrees Granted:	1
Invention disclosures citing ONR support:	0
Other funding sources:	1

Solidification Based Grain Refinement in Steels (Contract: 000140811052)

Objective:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

Plain 304

304 with 0.2% Rare Earth Addition

Approach:

Based on cyrstallographic and thermodynamic data, prospective phases were added to 304 and HK stainless steels. A series of thermal analysis experiments were then used to determine which phases actually reduced the undercooling required for freezing. Phases found to reduce undercooling in the thermal analysis experiments were then employed in a larger plate casting experiment series where tensile bars were created and strength-microstructure relationships were correlated.

Scientific or Naval Impact/ Results:

This project will result in a better understanding of how nucleation occurs in various steels. The enhanced understanding of steel nucleation will provide the opportunity to manipulate it , which will enable the development of stronger cast steels through grain refinement . The long term goal for this line of research is to develop technology that could be adopted by industry for the U.S. Navy for lighter and stronger ships, aircraft, and vehicles.

20110930007

Abstract

The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for the examined grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

Fiscal year 2011 was the final year for this project. Efforts centered on completing the final three tasks in the project (Tasks 7-9). An industrial trial on an investment casting was done using rare earth silicide additions in a furnace prior to pouring (Task 7). Some of the test parts had a finer structure than the baseline castings. A series of thermal analysis experiments were conducted to evaluate prospective heterogeneous nucleation phases (Task 8). Based on undercooling measurements several candidate phases had acted as effective nuclei. Plate castings using the heterogeneous nucleation phases identified by the thermal analysis experiments were created to provide a more detailed and industrially realistic experimental situation (Task 9). These plates were sectioned into tensile and metallographic samples. Most of the powder additions were ineffective at refining the microstructure or improving mechanical properties. Due to results from the previous work in plain carbon steels, rare earth and titanium additions were also examined. Rare earth additions were found in all cases to improve the ultimate tensile strength of 304, but not necessarily the yield strength. Titanium additions were found to be ineffective at the levels employed in this work.

Instructions: You may use this MS Word file as a guideline to submit the Technical Section (# 4) of the ONR End of Year Report. In this Technical Section, you are encouraged to include any images, tables, graphs, and equations that you feel may strengthen the technical quality of your report. The Technical Section must include the ***Objectives***, ***Approach***, **and** ***Progress*** completed since your last report. If this is a new effort or continuing work under an extension, the report should cover work completed during this FY. Please complete the ***Award Information*** section below so that technical information can be related to a specific award.

Please save the file using the award number as the file name (e.g. N0001496C0387.doc).

If you have any questions with this form or with the web site, please contact the help desk at Code_33_EOY_Report@ONR.NAVY.MIL

Award Information

Award Number	N000140811052
Title of Research	Solidification Based Grain Refinement in Steels
Principal Investigator	Dr. Robert Tuttle
Organization	Saginaw Valley State University

Technical Section

Technical Objectives

The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:

1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for the examined grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

Technical Approach

The wrought steel industry has successfully developed high strength low alloy (HSLA) grades of steel. Strength is developed in HSLA steels by thermomechanical grain refinement and precipitation hardening. This is achieved by precipitating niobium carbides, which pin the austenite grains and prevent grain growth during thermomechanical processing.[1-20] Strengthening is achieved by a Hall-Petch strengthening mechanism and precipitation hardening.[1-20] The thermomechanical grain refinement originally developed for these grades has also been adopted for other steel grades.[20] Unfortunately, steel castings cannot undergo thermomechanical grain refinement because they are produced near net shape. In many cases, steel foundries refine the structure of a casting through heat treatment. The energy required for grain refining via thermomechanical processes or heat treatment impacts the environmental friendliness and cost effectiveness of these grades. A better approach is to create a small grain structure by manipulating the solidification of steels. This will result in a processing route that both steel mills and steel foundries can use to improve properties. Also, alloys other than the traditional HSLA alloys, such as stainless steels, could be strengthened this way.

Solidification based grain refinement has been successfully employed in aluminum, copper, magnesium, and cast iron alloys. When metals solidify, there must be stable nuclei for grains to grow. There are two possible nucleation routes: homogenous nucleation, which requires a large amount of undercooling, and heterogeneous nucleation, which requires a foreign nuclei.[21] Homogeneous nucleation occurs in a metal when the melt has cooled enough to allow atomically small embryos to form in the melt. Formation of these embryos requires a significant driving force, because a high energy interface is created when they form. Heterogeneous nucleation occurs when new grains grow on foreign nuclei. Foreign nuclei are either introduced as a solid phase in the melt or as a phase that precipitates in the melt. To be effective, the foreign particle must remain solid long enough to nucleate a new grain, have a similar crystal structure to the desired phase, and have a favorable interfacial energy between the foreign particle and desired phase.[21-23] Unlike other metals, the melting temperature of steel makes it difficult to find a phase that has the required lattice parameter and a sufficiently high melting point to remain solid during solidification. Additionally, the solid state reactions that form ferrite, pearlite, and for some alloys, austenite make it difficult to identify the structure present just after solidification.

References

1. Zrnik, J., Kvackaj, T., Sripinproach, D., and Sricharoenchai, P., "Influence of plastic deformation conditions on structure evolution in Nb-Ti microalloyed steel", *Journal of Materials Processing Technology*, Vol 133, No 1-2, pp. 236-242, 2003.
2. Lottey, K. R., and Militzer, M., "Microstructure evolution in fine-grained microalloyed steels", *Materials Science Forum*, pp. 347-354, 2005.
3. Ghosh, A., Das, S., and Chatterjee, S., "Ultrahigh strength hot rolled microalloyed steel: Microstructure and properties", *Materials Science and Technology*, Vol. 21, No. 3, pp. 325-333, 2005.
4. Peter, J., Peaslee, K. D., and Panda, D. "Thermomechanical processing of HSLA wide-flange steel beams for increased core toughness", *Iron & Steel Technology*, Vol. 1, No. 7, pp. 172-180, 2004.
5. Fernandez, J.; Illescas, S.; Guilemany, J. M. "Effect of microalloying elements on the austenitic grain growth in a low carbon HSLA steel", *Materials Letters*, Vol. 61, No. 11-12, pp. 2389-2392, 2007
6. Chen, Guoan; Yang, Wangyue; Guo, Shouzhen; Sun, Zuqing. "Characteristics of microstructural evolution during deformation-enhanced ferrite transformation in Nb-microalloyed HSLA steel", *Journal of University of Science and Technology Beijing*, Vol. 14, No. 1,pp. 36-40, 2007.
7. Kang, J. S.; Huang, Y.; Lee, C. W.; Park, C. G., "Effect of thermo-mechanical process on the microstructure and mechanical properties of low carbon HSLA steels", *Advanced Materials Research*, Vol. 15-17,pp. 786-791, 2007.
8. Chakrabarti, Debalay; Davis, Claire; Strangwood, Martin, "Characterization of bimodal grain structures in HSLA steels", *Materials Characterization*, Vol. 58, No. 5,pp. 423-438, 2007.
9. Timokhina, I. B.; Hodgson, P. D.; Ringer, S. P.; Zheng, R. K.; Pereloma, E. V., "Precipitate characterisation of an advanced high-strength low-alloy (HSLA) steel using atom probe tomography", *Scripta Materialia*, Vol. 56, No. 7,pp. 601-604, 2007.

10. Hotta, S.; Murakami, T.; Narushima, T.; Iguchi, Y.; Ouchi, C., "Effects of cooling rate and direct hot deformation conditions after solidification on the austenitic microstructure evolved by simulated strip casting and thin slab casting processes in HSLA steels", *Advanced Materials Research*, Vol. 15-17,pp. 726-731, 2007.
11. Chen, Y. T.; Guo, A. M.; Wu, L. X.; Zeng, J.; Li, P. H., "Microstructure and mechanical property development in the simulated heat affected zone of V treated HSLA steels", *Acta Metallurgica Sinica*, Vol. 19, No. 1,pp. 57-67, 2006.
12. Megahed, Gamal; Paul, S. K.; Carboni, Andrea; Pigani, Alessandro; Piemonte, Carlo P., "The development of new steel grades and products: Casting and rolling of APIX70 grades for arctic applications in a thin slab rolling plant", *Proceedings of the McMaster Symposium on Iron & Steelmaking*, Vol. 33,pp. 292-300, 2005.
13. Alvarez, P.; Lesch, C.; Bleck, W.; Petitgand, H.; Schottler, J.; Sevillano, J. Gil., "Grain refinement of rapid transformation annealing of cold rolled low carbon steels", *Materials Science Forum*, Vol. 500,pp. 771-778, 2005.
14. Lottey, K. R.; Militzer, M., "Microstructure evolution in fine-grained microalloyed steels", *Materials Science Forum*, Vo. 500,pp. 347-354, 2005.
15. Zarandi, Faramarz; Yue, Steve., "Improvement of hot ductility in the Nb-microalloyed steel by high temperature deformation", *ISIJ International* (2005), Vol. 45, No. 5,pp. 686-693, 2005.
16. Khoo, C. A.; Fourlaris, G., "Control of grain size by second phase particle additions in novel HSLA strip steels", *Material Science & Technology 2004*, Vol. 1, pp. 21-29, 2004.
17. Gao, Wen; Garcia, C. I.; DeArdo, A. J., "The nucleation of ferrite from a coarse grained austenite during the slow continuous cooling of an HSLA steel," *Mechanical Working and Steel Processing Conference Proceedings*, Vol. 41, pp. 243-256, 2003.
18. Zhao, X. M.; Wu, D.; Zhang, L. Z.; Liu, Z. Y., "Modeling of isothermal precipitation kinetics in HSLA steels and its application", *Acta Metallurgica Sinica*, Vol. 17, No. 6,pp. 902-906, 2004.
19. Beres, Miloslav; Weirich, Thomas E.; Hulka, Klaus; Mayer, Joachim., "TEM investigations of fine niobium precipitates in HSLA steel", *Steel Research International*, Vol. 75, No. 11,pp. 753-758, 2004.
20. Peter, Joerg; Peaslee, Kent D.; Panda, Dhiren., "Thermomechanical processing of HSLA wide-flange steel beams for increased core toughness", *Iron & Steel Technology*, Vol. 1, No. 7,pp. 172-180, 2004.
21. Wallace, J.F., "Grain Refinement of Steels", *Journal of Metals*, pp. 372-376, 1963.
22. Form, G.W., and Wallace, J.F.," Solidification of Metals: General Principals", *Transactions of the American Foundrymen's Society*, Vol. 68, pp. 145-156, 1960.
23. Turnbull, G.K., Patton, D.M., Form, G.W., and Wallace, J.F., "Grain Refinement of Steel Castings and Weld Deposits", *Transactions of the American Foundrymen's Society*, Vol 69, pp. 792-804,1961.

Progress Statement Summary

Tasks 7 through 9 were the primary focus of fiscal year 2011 efforts. An industrial trial using 0.2% target rare earth (TRE) additions was conducted on a 1025 investment casting (Task 7). One casting on the test tree had a finer structure than the baseline casting; however, the other casting on the same tree had no observable microstructural differences. Analysis of the inclusions and fluid flow found the casting with no change had a more turbulent filling that resulted in inclusions with a different composition than the refined casting. Thermal analysis experiments using phases identified using crystallographic data as potential heterogeneous nuclei were performed in Task 8. These experiments examined the cooling profile of a test cup and the resulting microstructure of that cup. Several potential candidates were observed to reduce the undercooling required to initiate solidification. The final experimental series conducted during this fiscal year were plate castings (Task 9). Plate castings were produced with powder additions of the phases identified in Task 8. None of the powder addition plate castings produced a noticeable difference in microstructure or mechanical properties. Based upon experimental results from the plain carbon portion of the project, rare earth and titanium additions were examined. Titanium additions produced no noticeable changes. Rare earth additions increased ultimate tensile strength in all cases, and also improved yield strength in some cases.

Progress

As stated previously, the work performed during fiscal year 2011 centered on the final three tasks of the project. Those tasks were as follows:

Task 7 Conduct Industrial Trial
Task 8 Stainless Steel Thermal Analysis Experiments
Task 9 Stainless Steel Structure-Property Testing

Task 7 Conduct Industrial Trial

A test casting was selected based on its size and frequency of production (See Figure 1). The casting is part of a shipping container locking mechanism for container vessels and vehicles. The casting was poured from 1025 steel. Two castings are on each tree assembly. The investment casting shell was formed initially with a fine zircon wash followed by coarser silica slurries.

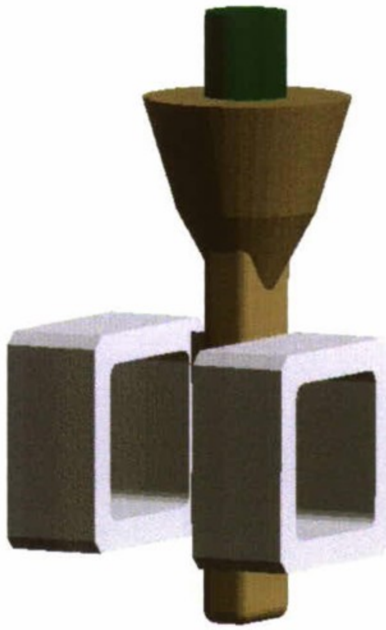


Figure 1 Test casting used in this work.

Melting was done in a 225kg capacity 3kHz coreless induction furnace. The test castings were poured at the end of a six casting batch. One test tree with no RE addition was poured. Before the second test tree was poured, sufficient RE silicide was added in the furnace for a target total rare earth (TRE) content of 0.2%. The chemical composition of the baseline and RE addition castings are listed in Table 1. The castings were poured at 1625°C. As is normal practice at this foundry, the castings were poured directly from the furnace. After pouring, the pouring basin was covered in an oxygen scavenger and the tree was placed in a metal container to prevent reoxidation of the steel.

Table 1 Experimental heat chemical analysis

Heat	C (%)	Si (%)	Mn (%)	P (%)	S(%)	Al (%)	Total RE (%)
1025	0.24	0.66	0.69	0.01	0.02	0.027	-
1025 -0.2% RE	0.23	.74	.67	0.01	0.01	0.023	0.04

Optical microscopy of the samples found a ferrite-pearlite structure in all the castings. Figure 2 depicts the microstructure for each casting in the trial. The ferrite grain size for the baseline casting was 35 μm ± 10 μm. Test Casting 1 had a similar structure to the baseline casting (See Figure 2). The measured ferrite grain size was 34 μm ± 6 μm. The ferrite grain size of Test Casting 2 was 27 μm ± 6 μm. Test Casting 2 had a wide distribution of ferrite grain sizes in it. The ferrite islands observable in Figure 2 typically consisted of several ferrite grains. There was also more fine, needle ferrite present in Test Casting 2. Most of the ferrite in the baseline and Test Casting 1 was composed of relatively large and uniform ferrite. No needle ferrite was observed in the baseline casting.

Baseline Casting Test Casting 1

Test Casting 2

Figure 2 Micrographs of the trial castings.

Examination of the samples with a scanning electron microscope (SEM) found a significant difference in the rare earth inclusions in the test castings. Rare earth inclusions in Test Casting 1 typically had a rare earth oxide center that was completely surrounded by an iron oxide phase (See Figure 3). Rare earth inclusions in Test Casting 2 typically contained only a rare earth oxide. Sometimes a small coating of an iron oxide phase was present, but none of the rare earth inclusions observed were completely contained by this phase. The difference in rare earth oxide structure and composition explains why refinement was present in only one casting. Since the rare earth inclusions in Test Casting 1 were coated with an iron oxide coating, they were unable to act as effective nuclei because there was no free surface for nucleation to occur on.

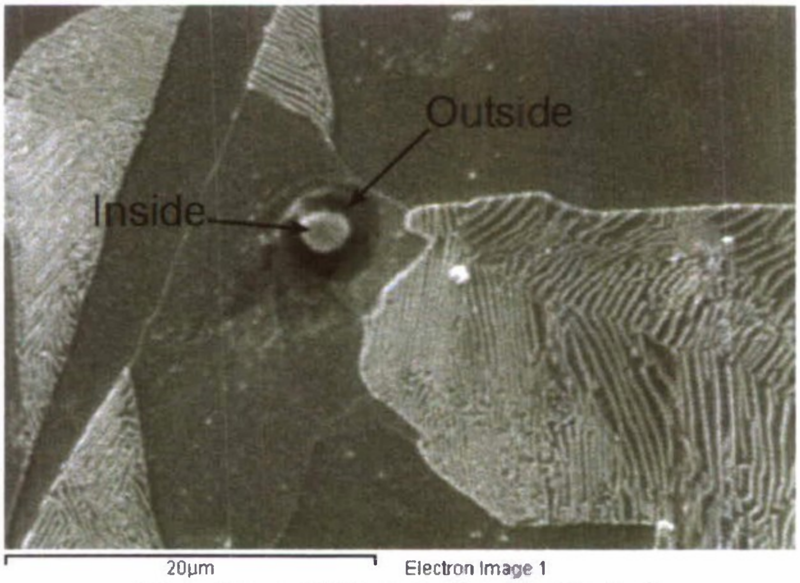


Figure 3 Typical RE inclusion from Test Casting 1

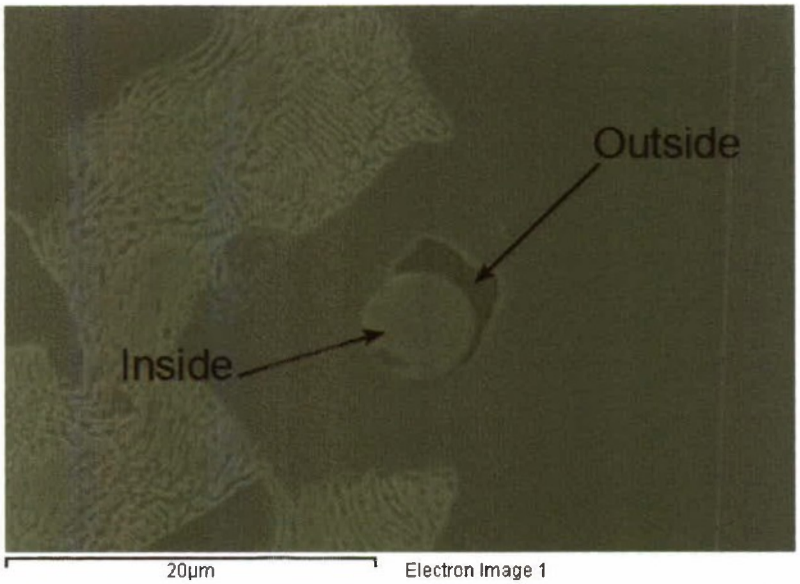


Figure 4 Electron micrograph of a typical inclusion from Test Casting 2.

Computer simulation of the casting revealed that one casting has a slightly more turbulent fill than the other. In fact, the upper in-gate on the left side of Figure 5 has relatively high velocities and significant air entrainment during most of the casting filling. This would result in significant reoxidation of the metal and would account for the presence of the iron oxide coatings observed on the rare earth inclusions in Test Casting 1.

Figure 5 Fluid fill at 307 ms (33% filled) into filling.

Task 8 Stainless Steel Thermal Analysis Experiments

A 23 kg heat of either 304 or HK steel were melted in a 3kHz induction furnace. The heat was brought to 1650°C (3000°F), and an oxygen activity measurement was made. Based on the oxygen level and a target residual aluminum content of 0.04%, the heat was deoxidized with aluminum shot. Table 2 lists the average chemical composition for each stainless steel composition. Five grams of high purity, -325 mesh test powder were placed in the thermal analysis (TA) cup (See Figure 6). The furnace was tapped into a 2.3 kg hand ladle. To maintain deoxidation, an additional 2.7g of aluminum wire were added per ladle. Liquid steel was poured into the TA cup and a data acquisition system (DAQ) recorded the cooling curve of the solidifying steel at a sampling rate of 12 Hz. Then, the TA cup was removed and the next cup and powder addition was inserted onto the TA stand. Each heat consisted of ten TA cups. The first and last cups contained no powder additions. This was done to guarantee no significant alloy or oxidation changes happened during the run. When the undercooling measurements between the first and last TA cups differed drastically, the entire heat was repeated. The experimental powder additions were then randomly ordered between the second and eighth TA cups. Each experimental powder addition was replicated three times. A total of fifteen TA cups were analyzed for each alloy.

Table 2 Average chemical composition of the heats.

Sample	C (wt. %)	Cr (wt. %)	Ni (wt. %)	Si (wt. %)	Mn (wt. %)	P (wt. %)	S (wt.%)	Al (wt. %)
304	0.07	17.7	8.24	0.30	1.69	0.023	0.002	0.01
HK	0.20	24.5	20.7	0.79	0.235	0.022	0.003	0.01

A

B

Figure 6 Thermal analysis setup used in this work. (A) The TA cup and test stand. (B) Overhead view of one of the TA cups.

The TA cups for this experimental setup consisted of a shell core cup with an S Type (Pt/10%Rh) thermocouple in the bottom of the cup (See Figure 6B). A quartz tube covered the thermocouple wire to protect it during filling. The cups were placed on a metal stand that connected them to the computer based DAQ system via S Type compensation wire (See Figure 6A). These TA cups are commercially available.

Powders for these experiments were selected based on their ability to nucleate either delta ferrite or austenite. Thermodynamic calculations were used to predict the initial phase to form upon solidification. 304 was expected to initially form delta ferrite at the start of solidification while HK formed austenite as the primary phase. Crystallographic data from the Pauling File was utilized to select candidate phases that would nucleate each alloy. MgO, NbO, NiAl, and TiC were selected for 304. La_2O_3, MgO, ZrO_2, and NbO were chosen for HK.

Figure 7 presents the measured undercooling for the 304 experiments. Every powder produced a reduction in undercooling compared to the no addition samples. NbO and TiN had the lowest and least spread in the undercooling measurements. Figures 8 and 9 show typical microstructures for the 304 samples. Secondary dendrite arm spacing (SDAS) measurements found no observable difference in the samples; except for the MgO addition samples which had a SDAS larger than the other samples. The reason for the lack of difference may have been due to the high cooling rates of the TA cups. While the powder additions assisted in initiating nucleation, dendrite growth during solidification and coarsening in the solid state may have been primarily controlled by the overall cooling rate. Such a mechanism does explain why the MgO samples had a larger SDAS since some of the MgO powder would float on top of the TA cup creating a slower cooling rate.

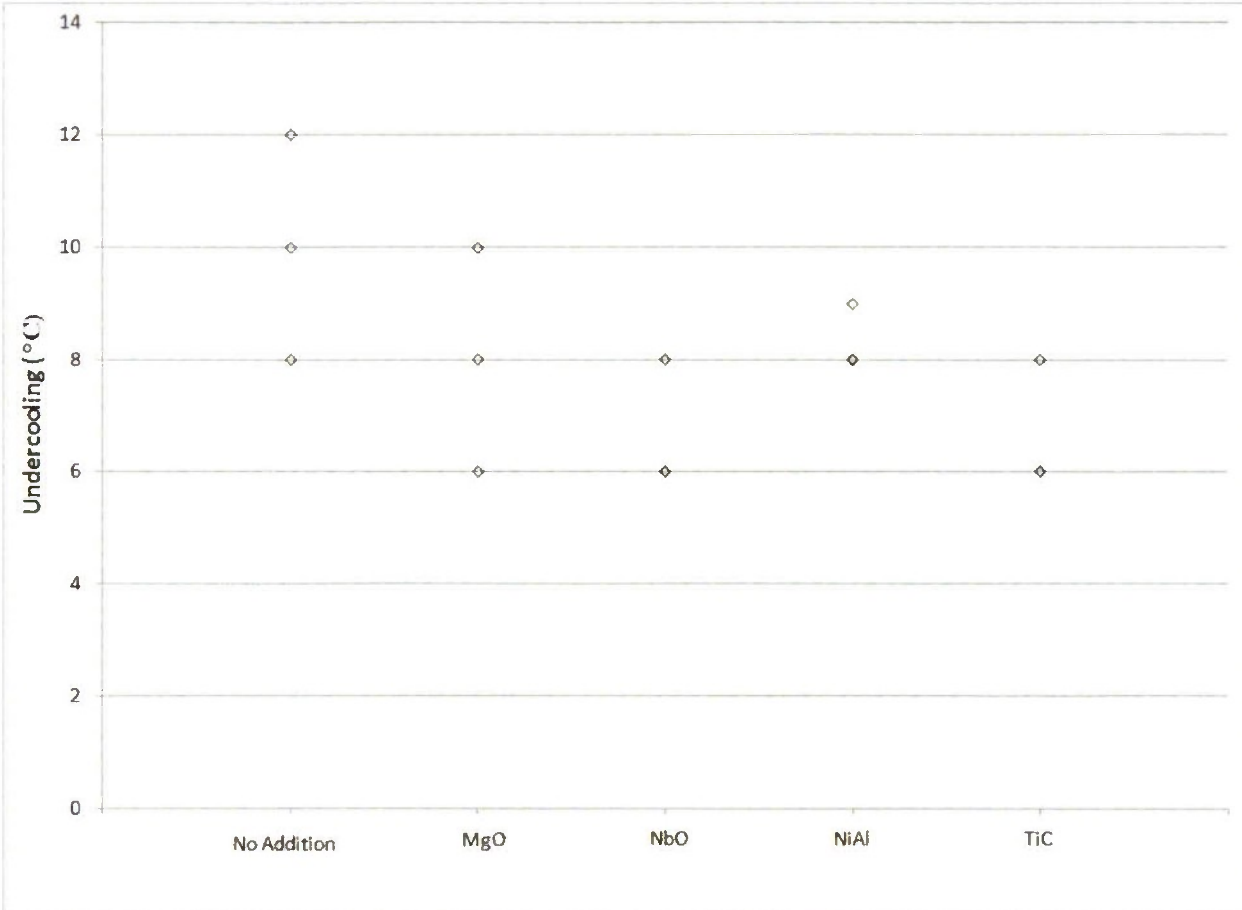


Figure 7 Undercooling measurements for the 304 samples.

Figure 8 Micrograph of the 304 sample with no addition.

Figure 9 Micrograph of the 304 sample with a NiAl addition.

Undercooling measurements for HK found a decrease for the La_2O_3, MgO, and NbO additions (See Figure 10). The lack of significant undercooling reduction was consistent with the PI's crystallographic calculations. Other researchers stated that ZrO_2 was an effective nuclei for austenite which was why it was included in this work.[1,2] On average ZrO_2 had a 15% disregistry with austenite. The lack of change in undercooling due to the ZrO_2 additions was consistent with these calculations. The other three powders all had a lattice disregistry less than 10%.

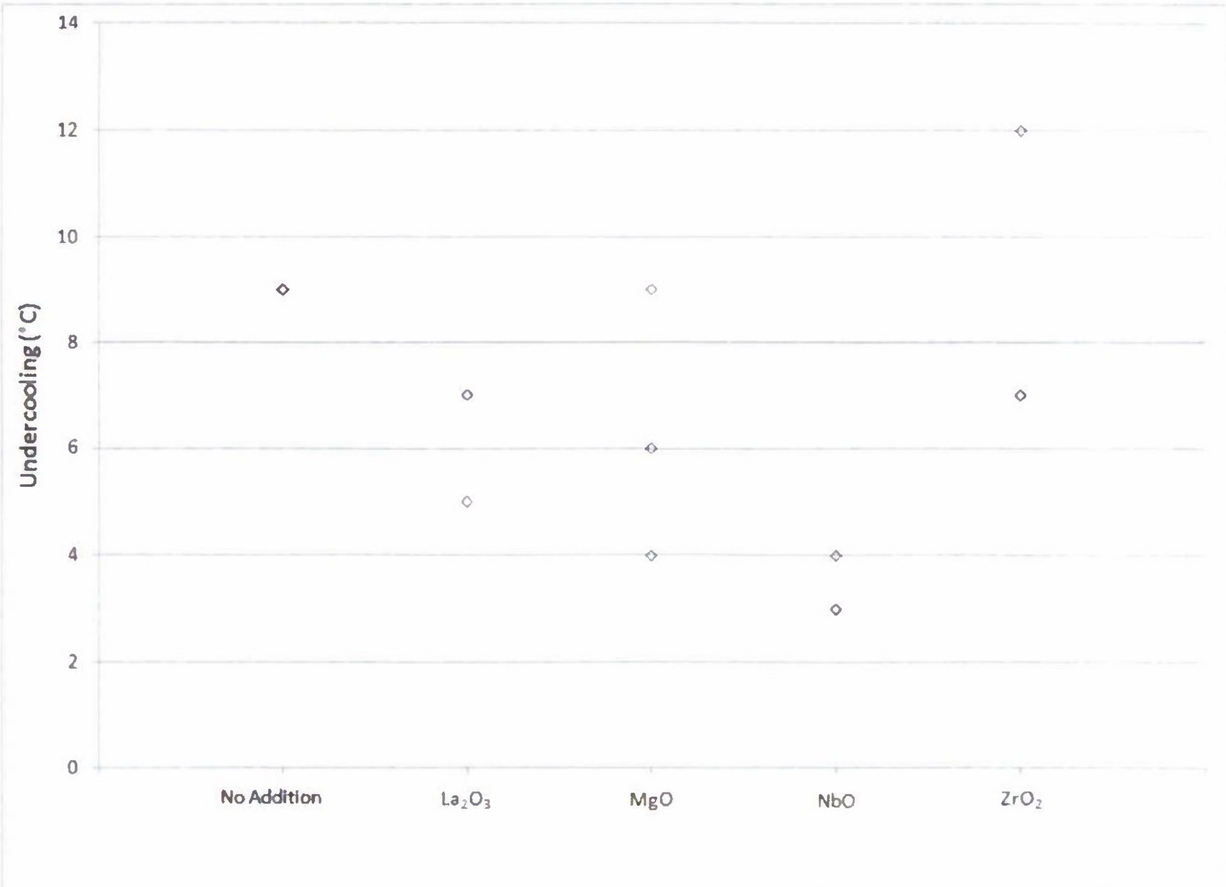


Figure 10 Undercooling measurements for the HK samples.

Figure 11 Representative micrograph of the no addition HK sample.

Figure 12 Micrograph of the HK sample with MgO powder addition.

References

1. Valdez, M. E., Shibata, H., Cramb, A. W., "Controlled Undercooling of Liquid Iron in Contact with ZrO_2 and MgO Substrates under Varying Oxygen Partial Pressure," *Metallurgical and Materials Transactions B*, vol. 37B, pp 959-965 (2006).
2. Suito, H., Ohta, H., Morioka, S., "Refinement of Solidification Microstructure and Austenite Grain by Fine Inclusion Particles," *ISIJ International*, vol. 46, no. 6, pp 840-846 (2006).

Task 9 Stainless Steel Structure-Property Testing

The goal of Task 9 was to understand refinement in a more industrially realistic experimental situation. Potential grain refiners identified in Task 8's thermal analysis experiments were selected for experimentation in plate castings. The PI also conducted a series of experiments with various rare earth additions and titanium additions.

A 23 kg heat of 304 was melted in an alumina lined, 3 kHz induction furnace in an air atmosphere. Part of the aluminum deoxidation addition was done in the furnace at 1650°C. The melt was brought to 1705°C prior to tapping into a preheated, fiber refractory lined ladle. Final aluminum deoxidation additions were added while the melt entered the ladle. Castings were poured at a target temperature of 1620°C. The castings were then allowed to cool below 530°C before being shaken out. After shakeout, the castings continued to cool until they reached room temperature.

Figure 13 represents the geometry of the plate casting and gating system used. Molds were manufactured using a clay bonded silica sand with an AFS GFN of 65, a clay content of 3.5%, and 2.4% water. The molds were compacted on a jolt/squeeze molding machine.

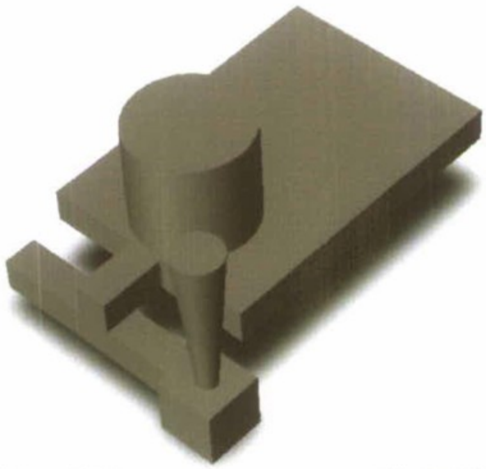
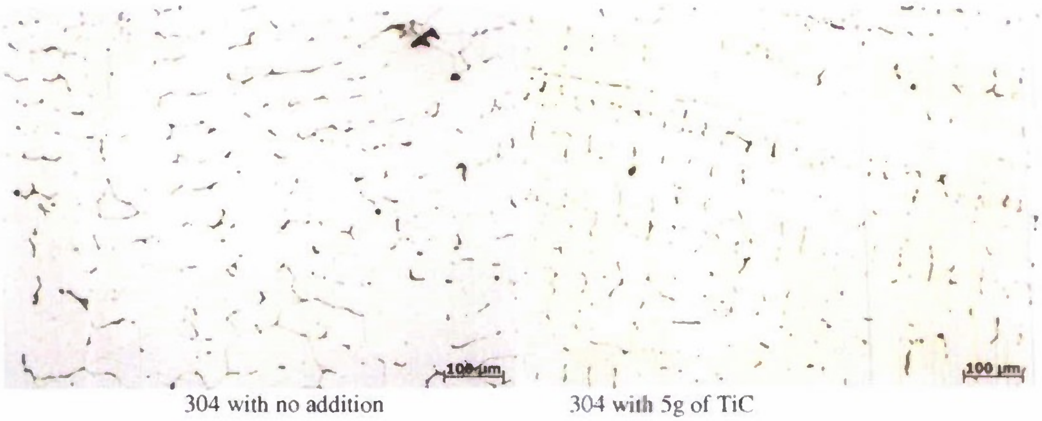


Figure 13 Plate casting geometry used in Task 9.

In the first series of experiments, powders of La_2O_3, MgO, NbO, NiAl, and TiN were added to the mold. Five grams of high purity, -325 mesh powder was poured into the down sprue as the casting was poured. No powder additions were successful at affecting the structure of 304 stainless steel (See Figure 14). This was similar to the problems with the powder additions from the plain carbon experiments. There are two possible causes: particle dissolution or ineffective entrainment. While there is incomplete thermodynamic data to determine if particle dissolution is true in all cases, NbO, NiAl, and TiC are predicted by thermodynamic calculations to dissolve into molten steel which would make them unavailable as heterogeneous nuclei. This theory does not explain the lack of refinement with the addition of MgO or La_2O_3. Another possibility is that despite the turbulent nature of the flow within the downsprue there was insufficient entrainment of the particles. If insufficient particles entered the plate cavity portion of the mold then effective heterogeneous nucleation may not have been able to happen. This would explain why none of the particle additions produced refinement, and is the PI's current theory on why these experiments did not produce any differences.



304 with no addition 304 with 5g of TiC

Figure 14 Micrographs from the plate castings with powder additions.

Based on work in the plain carbon steels and the theory that the particles added in the powder addition experimental series were not evenly distributed in the melt, the PI conducted experiments with ferrotitanium additions. The premise was that it may be necessary to form titanium carbonitrides insitu. The melting and molding procedures outlined above were also used in these experiments. However instead of adding powders into the pouring stream, a ferrotitanium addition was done in the ladle during tapping. Target titanium levels of 0, 0.1%, and 0.2% were utilized. Due to misrun and cold lap defects in the first castings, the silicon content had to be increased to 0.4%. Table 3 lists the composition of the three heats. Figure 15 presents the yield strength and ultimate tensile strength (UTS) measurements for this work. The 304 with 0.1% Ti has a lower yield strength than the other alloys tested. This is probably due to the much lower carbon content of this material. The baseline 304 and the 304 with 0.2% Ti materials had approximately equal yield strengths. The UTS for all three castings were also similar. Microstructural investigation found no significant difference in grain size. This supports the theory that the cause of the lower yield strength in the 304 w/ 0.1% Ti material was due to a difference in carbon content.

Table 3 Average chemical composition of the heats.

Sample	C (wt.%)	Cr (wt.%)	Ni (wt.%)	Si (wt.%)	Mn (wt.%)	P (wt.%)	S (wt.%)	Ti (wt.%)	Al (wt.%)
304	0.23	18	7.7	0.44	2.1	0.03	0.007	-	0.058
304 w/ 0.1 Ti	0.059	16	8.2	0.41	1.6	0.02	0.002	0.04	0.012
304 w/ 0.2 Ti	0.18	16	7.8	0.52	2.3	0.02	0.004	0.08	0.032

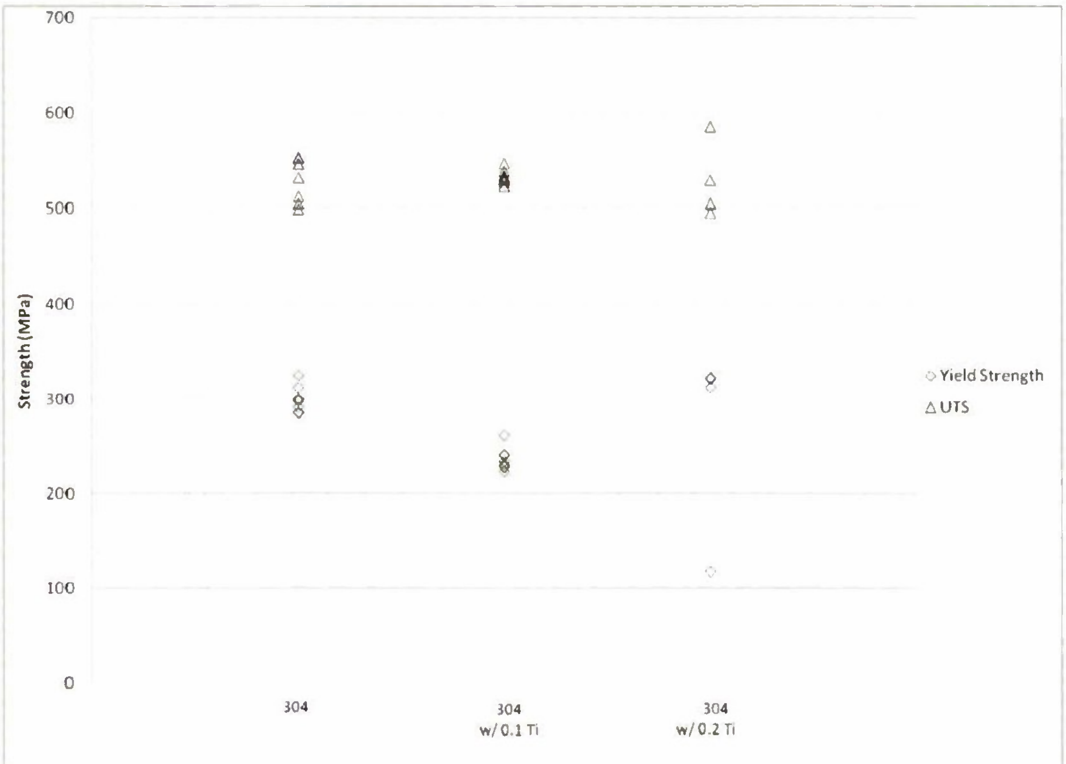


Figure 15 Yield strength and UTS for titanium containing 304 castings.

In the last series of experiments conducted, rare earth additions to 304 using either misch metal or rare earth silicide were done. Like the titanium work, the concept behind these experiments was to precipitate rare earth oxides within the steel. This assists with creating a uniform distribution of rare earth oxides, which can act as heterogeneous nuclei. Target rare earth contents of 0, 0.1%, and 0.2% were used. Additions of either rare earth silicide or misch metal were added in the ladle during tapping.

Figure 16 illustrates the yield strength and UTS measurements from these experiments. The UTS for all of the steels with rare earth additions were higher than the baseline material. The 0.1% RE and 0.1% Ce samples had yield strengths similar to the baseline material. The 0.2% RE and 0.2% Ce samples had a yield strength approximately ten percent higher.

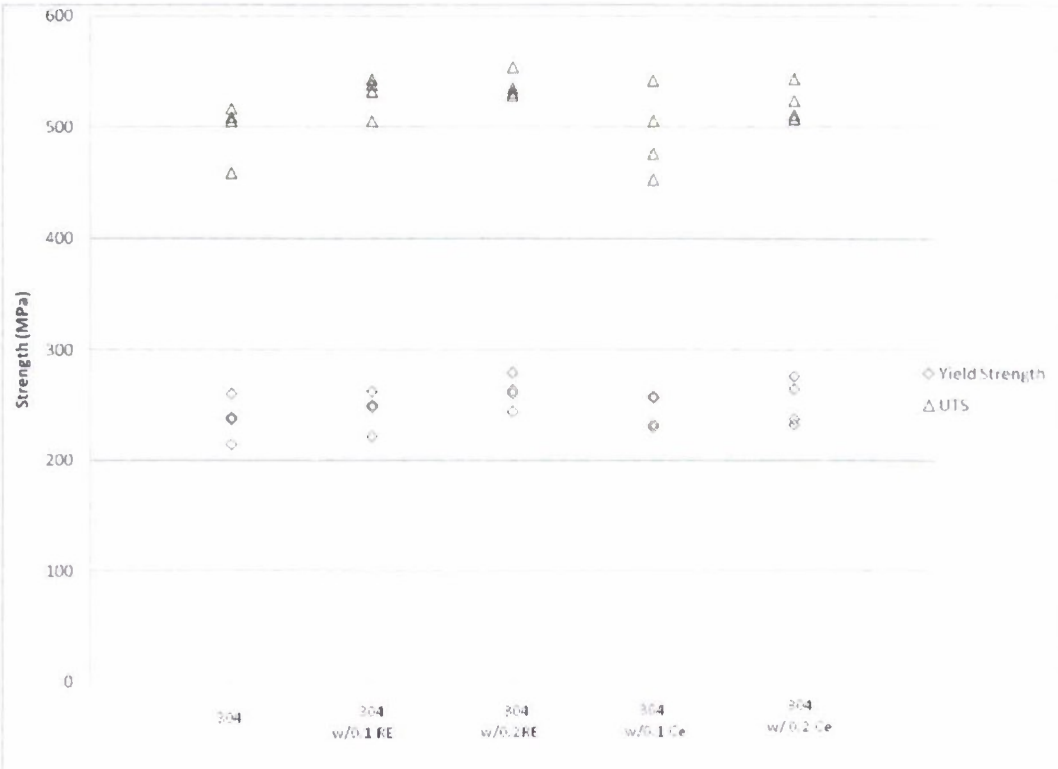
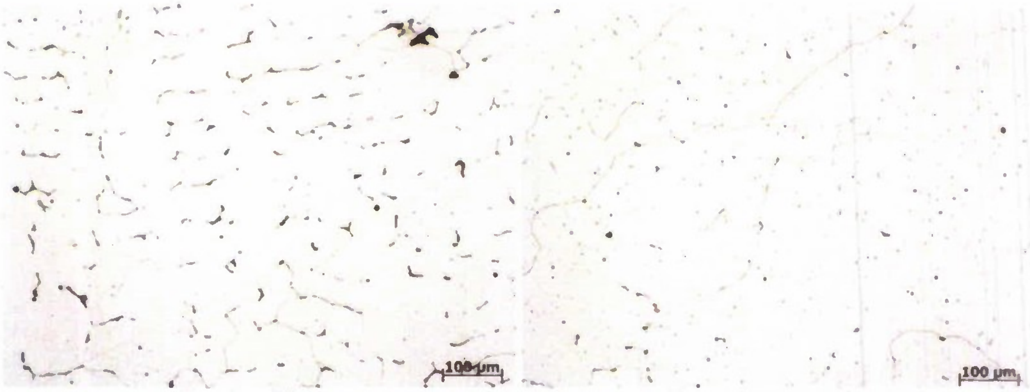


Figure 16 Strength of 304 steels with rare earth silicide (RE) or misch metal (Ce) additions.

Microstructural examination found that all of the rare earth addition samples had a finer grain size than the baseline material (See Figures 17 and 18). SEM investigation of the inclusions within the rare earth steels found no significant difference between the rare earth oxide inclusions. None of the inclusions were surrounded by an iron oxide phase, which meant they were all available for nucleation. The difference in yield strength is not completely explained by a simple grain size reduction mechanism because the 0.1%RE and 0.1%Ce samples have a similar grain size to the 0.2% RE and 0.2% Ce samples (See Figure 18). It is possible that excess cerium entered into the matrix and provided solid solution strengthening that caused the observed increase in yield strength. Another possible mechanism is that more inclusions formed in the higher rare earth content steels and these inclusions reinforce the grain boundaries of the steel which provided higher strength. There is insufficient evidence at this time to draw a clear and consistent theory on the observed property/microstructure relationship. The PI plans on continuing to examine the data until a satisfactory theory can be proposed.



Baseline 304 | 304 w/ 0.2% RE addition

Figure 17 Typical micrographs from the rare earth addition experiments.

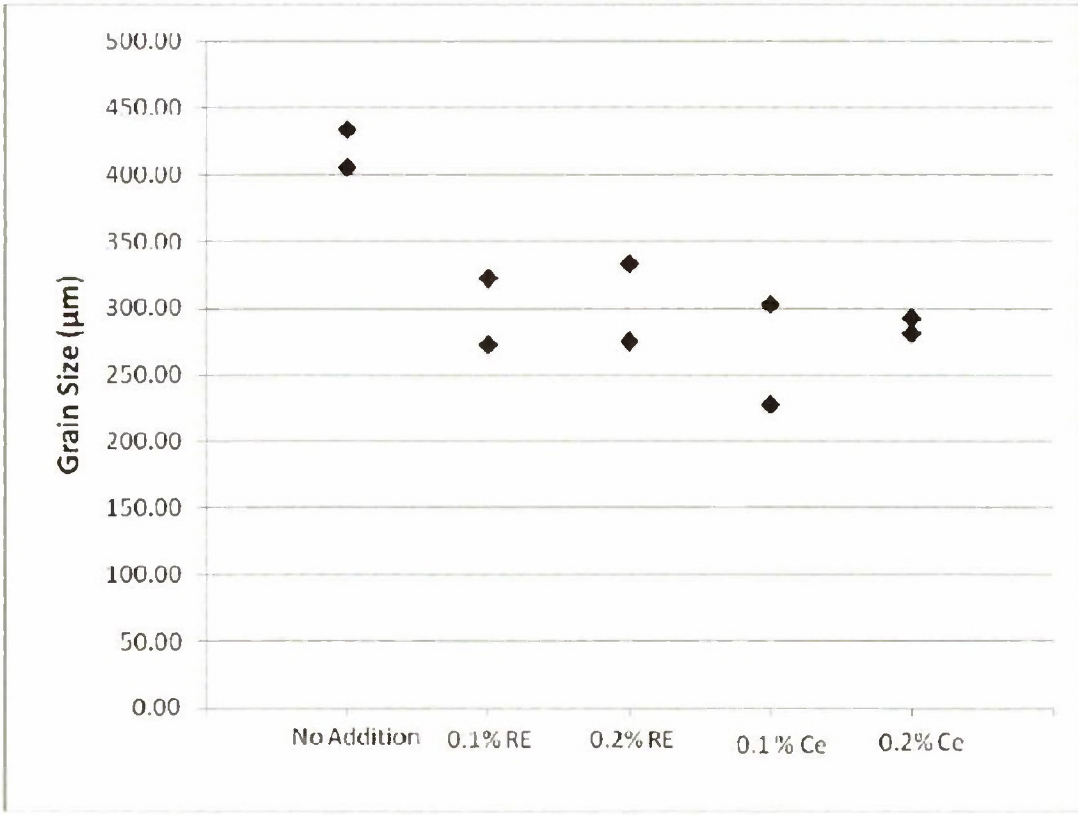


Figure 18 Average grain size for each steel.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
27-09-2011	Performance/Technical Reports for FY 2011	01-07-2010 - 30-06-2011

4. TITLE AND SUBTITLE
Solidification Based Grain Refinement in Steels

5a. CONTRACT NUMBER
N00014-08-1-1052

5b. GRANT NUMBER
N00014-08-1-1052

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Tuttle, Robert

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Saginaw Valley State University
7400 Bay Road
University Center, MI 48710

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ONR Reg. Office Chicago - N62880
230 South Dearborn, Room 380
Chicago, IL 60604-1595

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Pubic Release; distribution is Unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The overall research objective of this project is to determine suitable grain refiners for cast steels. Specific objectives are:
1) Identify possible phases to grow delta ferrite and austenite using current nucleation theory, crystallographic data, and thermodynamics.
2) Experimentally verify the effectiveness of possible nucleating compounds.
3) Extend grain refinement theory and solidification knowledge through experimental data.
4) Determine structure property relationships for the examined grain refiners.
5) Formulate processing techniques for using grain refiners in the steel casting industry.

15. SUBJECT TERMS
steel, casting, foundry, grain refinement, mechanical properties, solidification, and heterogeneous nucleation

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
u	u	u	UU	10 double-sided pages + SF298	Robert Tuttle
					19b. TELEPONE NUMBER (*Include area code*) 989-964-4676